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<b>(54) Title:</b> TREATMENT OF ZEOLITE TO IMPROVE ITS BUTENE SELECTIVITY  <b>(57) Abstract</b>  A medium pore zeolite cracking catalyst is treated with steam followed by treatment with an acidic solution to improve its butene selectivity in catalytic cracking. A process for using the treated medium pore cracking catalyst in a fluidized catalytic cracking process is also disclosed.		

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TREATMENT OF ZEOLITE TO IMPROVE ITS BUTENE SELECTIVITY

This invention relates to a process for treating a medium-pore zeolite to improve its butene selectivity in catalytic cracking.

In fluidized catalytic cracking (FCC) processes, a relatively heavy hydrocarbon feedstock, e.g., a gas oil, admixed with a suitable cracking catalyst to provide a fluidized suspension, is cracked in an elongated reactor, or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The reaction products and spent catalyst are discharged from the riser into a separator, e.g. a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a product recovery zone and the spent catalyst entering a dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbon product from the spent catalyst prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst where it desorbs such hydrocarbons conveying them to the product recovery zone. The fluidizable catalyst is continuously circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which is endothermic.

The use of medium pore zeolites, such as ZSM-5, in conjunction with a large pore zeolite cracking catalyst of the X or Y faujasite variety is described in U.S. Patent Nos. 3,894,931; 3,894,933; and 3,894,934.

It has now been found that pretreatment of a medium pore zeolite catalyst by steaming and acid treatment has an unexpected effect on its butene selectivity in catalytic cracking processes.

The invention therefore includes a process for increasing the butene selectivity of a cracking catalyst comprising a crystalline aluminosilicate zeolite having a Constraint Index of 1 to 12, which process comprises

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steaming said zeolite after calcination and contacting the steamed zeolite with an acidic solution.

5 The invention further includes a process for the catalytic cracking of a hydrocarbon by contact of said hydrocarbon with a catalytic cracking catalyst, comprising a calcined medium pore crystalline aluminosilicate zeolite, wherein said zeolite has been pretreated by steaming and contacting the steamed zeolite with an acidic solution.

10 The process of the present invention involves treatment of a medium pore zeolite, such as ZSM-5, with an acidic solution after steaming to improve butene selectivity in catalytic cracking. The zeolite is calcined prior to steaming.

15 A convenient measure of the extent to which a zeolite provides control of access to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. Zeolites which provide a highly restricted access to and egress from its internal structure have a high value for the Constraint Index, and zeolites of this kind usually have pores of small size, e.g. less than 5 Angstroms. On the other hand, zeolites which provide relatively free access to the internal zeolite structure have a low value for the Constraint Index, and usually have pores of large size, e.g. greater than 8 Angstroms. The method by which  
20 Constraint Index is determined is described fully in U.S. Patent No. 4,016,216.

The crystalline aluminosilicate zeolites useful herein are medium pore zeolites. Medium pore zeolites generally have a Constraint Index of 1-12.

30 Constraint Index (CI) values for some typical medium pore zeolites useful in the process of the invention are:

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CI (at test temperature)

	ZSM-5	6-8.3	(371°C-316°C)
	ZSM-11	5-8.7	(371°C-316°C)
5	ZSM-12	2.3	(316°C)
	ZSM-22	7.3	(427°C)
	ZSM-23	9.1	(427°C)
	ZSM-35	4.5	(454°C)
	ZSM-38	2	(510°C)
10	ZSM-48	3.5	(538°C)
	ZSM-50	2.1	(427°C)
	TMA Offretite	3.7	(316°C)
	Clinoptilolite	3.4	(510°C)
	Zeolite Beta	0.6-2.0	(316°C-399°C)

15

Preferred zeolites for use in the present process include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-48. ZSM-5 is particularly preferred.

20 ZSM-5 is described in greater detail in U.S. Patent Nos. 3,702,886 and Re. 29,948.

ZSM-11 is described in greater detail in U.S. Patent No. 3,709,979.

ZSM-12 is described in U.S. Patent No. 3,832,449.

ZSM-22 is described in U.S. Patent No. 4,556,477.

25 ZSM-23 is described in U.S. Patent No. 4,076,842.

ZSM-35 is described in U.S. Patent No. 4,016,245.

ZSM-48 is more particularly described in U.S. Patent No. 4,234,231.

30 The zeolite is calcined in air or other inert gas at temperatures ranging from 200°C to 900°C for periods of time from 1 to 48 hours or more.

It has been found in accordance with the present invention that catalysts of improved selectivity for butenes are obtained by subjecting the calcined zeolite to a steam treatment followed by acid treatment. Preferably, 35 the starting zeolite has a silica/alumina ratio of less than about 200:1.

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The steam treatment is conducted at elevated temperatures in the range of 425 to 870°C (800 to 1600°F) and preferably in the range of 540 to 815°C (1000 to 1500°F) and at a water partial pressure of 13 to 200 kPa (100 to 1500 torr). The treatment may be accomplished with an atmosphere comprising 5 to 100% steam. The steaming is carried out for a period in the range of from 0.5 to 12 hours.

Following steaming the zeolite is contacted with an acidic solution. Typical inorganic acids which can be employed include mineral acids such as hydrochloric, sulfuric, nitric and phosphoric acids, peroxydisulfonic acid, dithionic acid, sulfamic acid, peroxymonosulfuric acid, amidodisulfonic acid, nitrosulfonic acid, chlorosulfonic acid, pyrosulfonic acid, and nitrous acid. Representative organic acids which may be used include formic acid, oxalic acid, trichloroacetic acid and trifluoroacetic acid. Hydrochloric acid and nitric acid are preferred.

The acid treatment is conducted at a temperature in the range of 35 to 120°C (100 to 250°F). The acid treatment is carried out for a period in the range of 1 to 36 hours. The treatment may be accomplished with an acidic solution having a pH less than 4.

It may be desired to incorporate the zeolite with another material which is resistant to the temperatures and other conditions employed in the present process. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the zeolite, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitably

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serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into  
5 naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e., clays, oxides, etc., function as binders for the catalyst. It is  
10 desirable to provide a catalyst having good crush strength because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

Naturally occurring clays which can be composited with  
15 zeolite crystals include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or  
20 anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the zeolite also include inorganic oxides, notably alumina.

25 In addition to the foregoing materials, the crystals can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-  
30 zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. It may also be advantageous to provide at least a part of the foregoing matrix materials in colloidal form so as to facilitate extrusion of the bound catalyst component(s).

35 The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal content ranging from 1 to 90 percent by weight and

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more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

5 The cracking catalyst comprising the medium pore zeolite pretreated in accordance with the invention will also normally contain a large pore cracking catalyst having a constraint index less than 1 such as zeolite X or Y. The large pore zeolite may be combined with the same matrix as the medium pore zeolite (so that a single catalyst particle  
10 contains both zeolites) or may be combined with a separate matrix (so that each zeolite is contained by a separate catalyst particle).

Hydrocarbon charge stocks undergoing cracking in accordance with this invention comprise hydrocarbons  
15 generally and, in particular, petroleum fractions having an initial boiling range of at least 200°C (400°F), a 50% point range of at least 260°C (500°F) and an end point range of at least 315°C (600°F). Such hydrocarbon fractions include gas oils, residual oils, cycle stocks,  
20 whole top crudes and heavy hydrocarbon fractions derived by the destructive hydrogenation of coal, tar, pitches, asphalts and the like. As will be recognized, the distillation of higher boiling petroleum fractions above about 400°C (750°F) must be carried out under vacuum in  
25 order to avoid thermal cracking. The boiling temperatures utilized herein are expressed in terms of convenience of the boiling point corrected to atmospheric pressure.

Catalytic cracking, in which the catalysts of the invention are employed, embraces operational conditions  
30 including temperature ranges of 400°F (204°C) to 1200°F (649°C) and reduced, atmospheric or super atmospheric pressures. The catalytic cracking process may be operated batchwise or continuously. The catalytic cracking process can be either fixed bed, moving bed or fluidized bed. The  
35 hydrocarbon chargestock flow may be either concurrent or countercurrent to the catalyst flow. The process of the



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invention is particularly applicable to fluid catalytic cracking (FCC) processes.

Briefly, in the FCC process, the catalyst is in the form of microspheres, which act as a fluid when suspended in oil vapor or gas. The hydrocarbons contact the fluidized catalysts and are catalytically cracked to lighter products. Deactivation of the catalyst by coke necessitates regeneration of the coked catalyst in the regenerator of an FCC unit. Although the design and construction of individual FCC units can vary, the essential elements of an FCC unit are illustrated in U.S. Patent No. 4,368,114.

The treatment process of the present invention results in at least about a 3% increase in the  $C_4/C_3$  ratio and preferably at least about a 10% increase in the  $C_4/C_3$  ratio. In refineries where butene is more valuable than propene, the impact of the process of the present invention is significant.

The treatment process of the present invention further results in an increase in gasoline selectivity since there is a correlation between  $C_4/C_3$  selectivity and gasoline selectivity. A ZSM-5 FCC additive is gasoline selective if it causes little gasoline yield loss per octane gain.

The invention will now be more particularly described with reference to the Examples and the accompanying drawings, in which:

Figure 1 is a graphical illustration of the  $C_4/C_3$  selectivity using the steamed ZSM-5 of Example 2 in comparison to the steamed/acid treated ZSM-5 of Example 3.

Figure 2 is a graphical illustration of the  $C_4/C_3$  selectivity using the steamed ZSM-5 of Example 5 in comparison to the steamed/acid treated ZSM-5 of Example 6.

#### Example 1

A steam treated catalyst is prepared by steaming a calcined, unbound ZSM-5 with 100% steam at 760°C (1400°F) and 1 atmosphere (100 kPa) pressure for 5 hours. The

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steamed ZSM-5 has an Si/Al ratio of about 60 and an average particle size of about 0.5 micron.

#### Example 2

5           A 1:1 mixture of 1-hexene and 1-octene is  
representative of a mixture of gasoline range ( $C_5$ - $C_{12}$ )  
olefins found in FCC feedstocks. The 1:1 hexene/octene  
mixture is reacted over the catalyst of Example 1 at 540°C  
(1000°F) and a pressure of about 1.1 atm (111 kPa). The  
10       hydrocarbon feed partial pressure is about 0.4 atmospheres  
(40 kPa) and a nitrogen carrier gas is also used. The flow  
rate is varied to obtain conversions of the hexene/octene  
feed to  $C_5$ - products in the range of 20 to 50%.  
Conversions, the yields of propene and butene and the  $C_4/C_3$   
15       ratio are shown below in Table 1.

#### Example 3

The catalyst of Example 1 is refluxed in 0.5 N HCl for  
24 hours, filtered and dried. The catalyst is then used to  
20       crack the hexene/octene feed mixture as set forth in  
Example 2. Conversions, the yields of propene and butene  
and the  $C_4/C_3$  ratio are shown below in Table 1.

#### Example 4

25           A steam treated ZSM-5 catalyst is prepared in the same  
manner as Example 1. The steamed ZSM-5 has an Si/Al ratio  
of about 60 and an average particle size of about 0.1  
micron.

#### Example 5

30           A 1:1 hexene/octene mixture is reacted over the  
catalyst of Example 4 in the same manner as Example 2.  
Conversions, the yields of propene and butene and the  $C_4/C_3$   
ratio are shown below in Table 1.

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Example 6

The catalyst of Example 5 is refluxed in 0.5 N HCl for 24 hours, filtered and dried. The catalyst is then used to crack the hexene/octene feed mixture as set forth in Example 2. Conversions, the yields of propene and butene and the  $C_4/C_3$  ratio are shown below in Table 1.

TABLE 1

	<u>Sample</u>	<u>C<sub>6</sub>+ Conv. Wt%</u>	<u>Propene Yield, Wt%</u>	<u>Butene Yield, Wt%</u>	<u>C<sub>4</sub>/C<sub>3</sub></u>
15	Example 2	31.2	9.2	11.6	1.26
	Example 2	45.0	14.2	16.3	1.15
	Example 2	48.6	15.6	17.5	1.12
	Example 2	54.5	17.8	19.4	1.09
20	Example 3	31.7	9.1	12.0	1.32
	Example 3	39.2	11.3	14.8	1.31
	Example 3	52.4	16.5	19.1	1.16
25	Example 5	18.8	5.6	7.0	1.25
	Example 5	45.5	14.3	16.8	1.17
	Example 5	52.7	17.2	19.1	1.11
30	Example 6	17.0	4.5	6.7	1.49
	Example 6	40.3	11.5	15.7	1.37
	Example 6	53.2	16.5	19.9	1.21

The process of the present invention maximizes the  $C_4/C_3$  ratio. Figure 1 compares  $C_4/C_3$  ratios for the catalyst of Example 1 before and after the acid treatment. Figure 2 compares the  $C_4/C_3$  ratios for the catalyst of Example 4 before and after acid treatment. Table 1 shows that the acid treatment results in an increase in the butene selectivity. It is believed that the non-framework alumina generated during steaming partially blocks the transport of species in the zeolite crystal, resulting in lower butene selectivity. The acid treatment, however, removes at least part of this alumina with a concomitant increases in butene selectivity.

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## Claims:

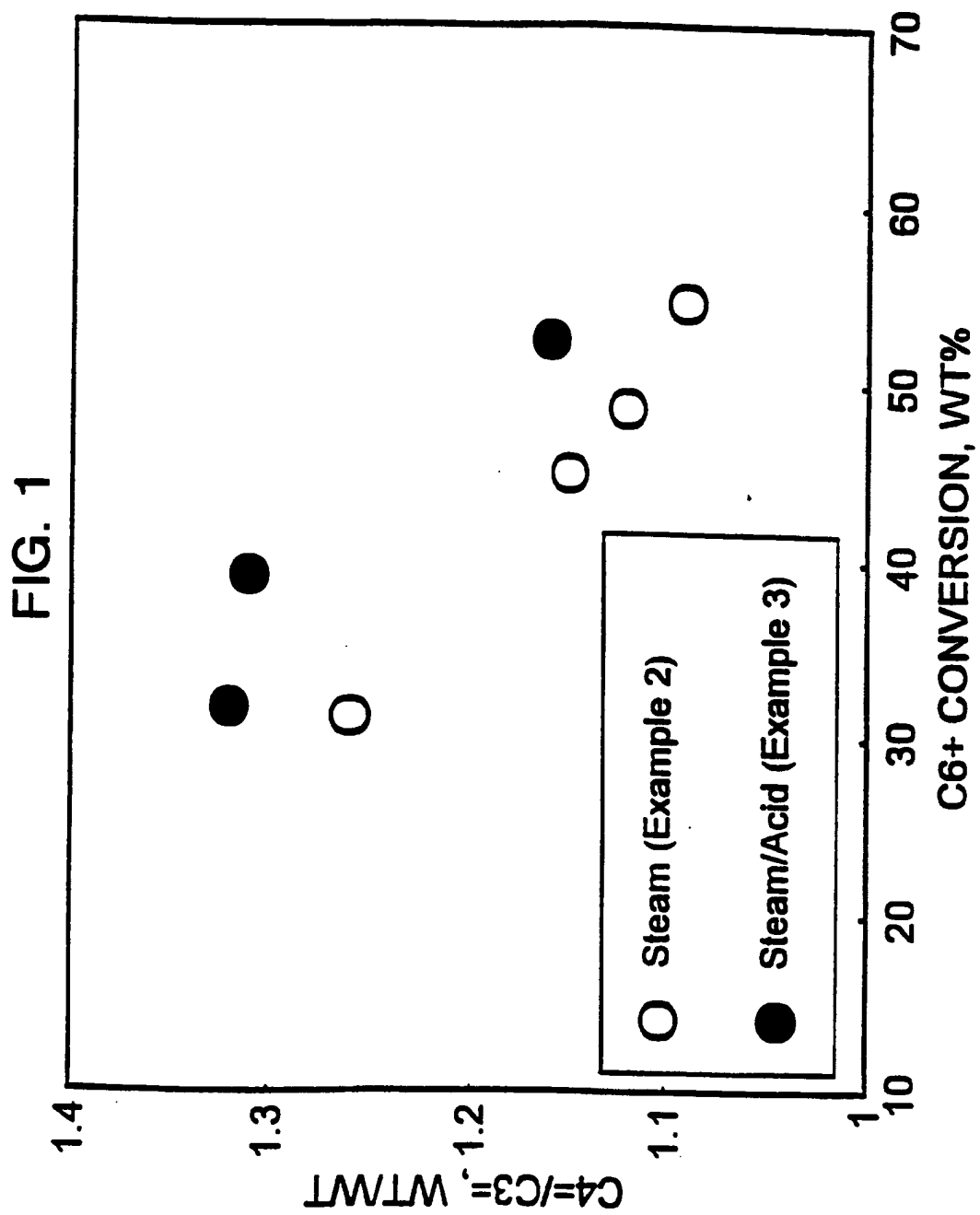
1. A process for increasing the butene selectivity of a cracking catalyst comprising a crystalline aluminosilicate zeolite having a Constraint Index of 1 to 12, which process comprises steaming said zeolite after calcination and contacting the steamed zeolite with an acidic solution.
2. The process of claim 1, wherein said crystalline aluminosilicate zeolite is selected from ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, and ZSM-48.
3. The process of claim 1, wherein said crystalline aluminosilicate zeolite is ZSM-5.
4. The process of claim 1, wherein the starting zeolite has a silica/alumina ratio of less than about 200:1.
5. The process of claim 1, wherein said acidic solution comprises a mineral acid.
6. The process of claim 1, wherein said acidic solution comprises hydrochloric acid.
7. The process of claim 1, wherein said acidic solution has a pH of less than about 4.
8. The process of claim 1, wherein steaming conditions include a water partial pressure of 13 to 200 kPa (100 to 1500 torr); a temperature in the range of 540 to 815°C (1000 to 1500°F); and a contact time in the range of 0.5 to 12 hours.

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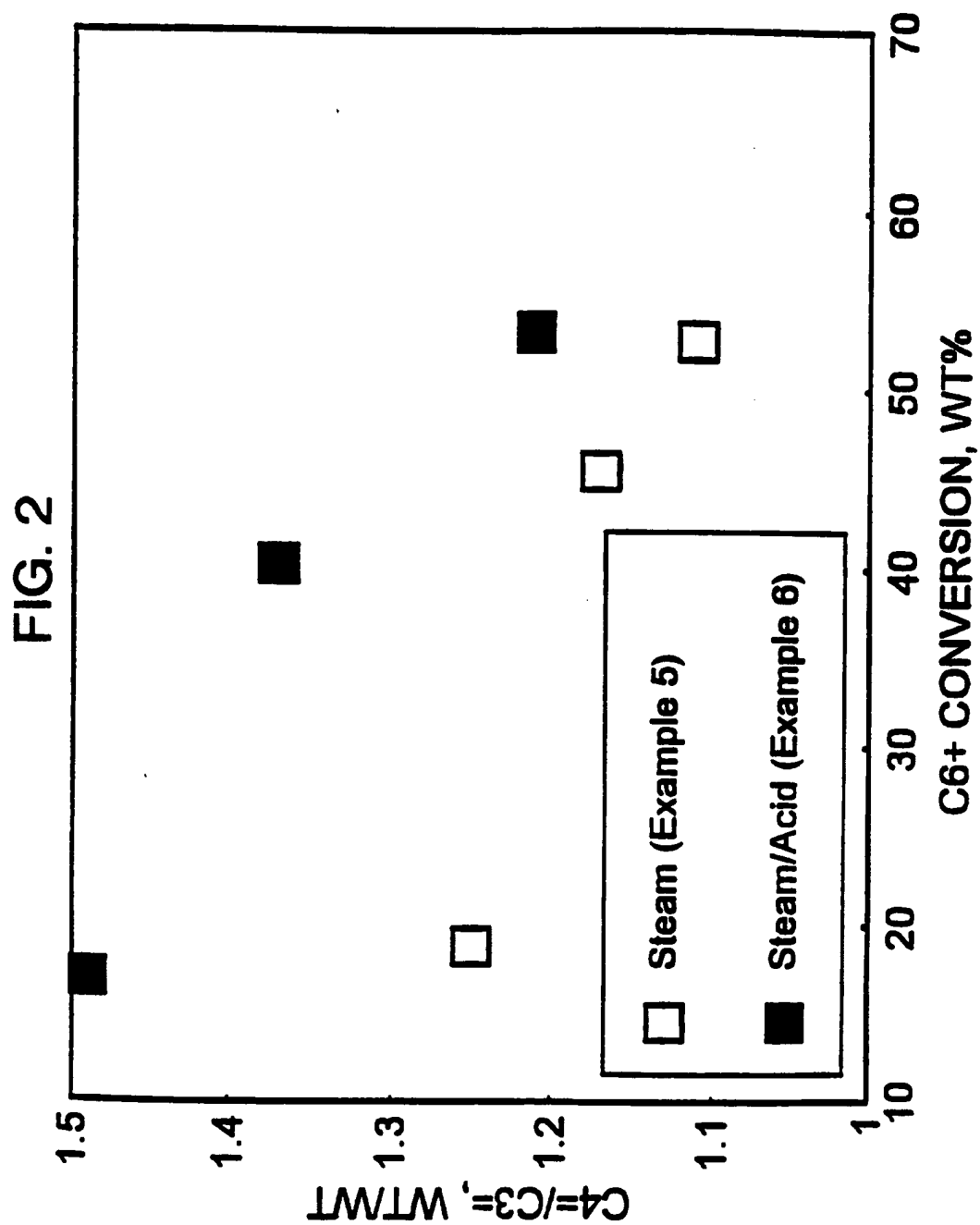
9. A process for the catalytic cracking of a hydrocarbon by contact of said hydrocarbon with a catalytic cracking catalyst, comprising a calcined medium pore crystalline aluminosilicate zeolite, wherein said zeolite  
5 has been pretreated by steaming and contacting the steamed zeolite with an acidic solution.

10. The process of claim 9, wherein the catalyst also includes a large pore cracking component.  
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/11705

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 38/60, 38/06, 29/06; C10G 11/05

US CL :502/27, 55, 77, 85; 208/113, 120

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/27, 55, 77, 85; 208/113, 120

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS-search terms: zeolite, acid treat7, calcine and steam and acid,

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,943,545 (CHANG ET AL.) 24 July 1990, col. 1, lines 16-18 and 50-68; col. 2, lines 1-38; col. 3, line 52 through col. 6, line 8; col. 6, lines 41-46; and claim 1.	1-10
X	US, A, 5,151,391 (FU ET AL.) 29 September 1992, col. 1, lines 33-56; col. 2, lines 3-40 and 63-68; col. 3, lines 1-15 and 32-68; col. 4, lines 1-16; and col. 5, line 24 through col. 6, line 38.	1-10
A	US, A, 3,684,738 (CHEN) 15 August 1972.	1-10
A	US, A, 4,356,338 (YOUNG) 26 October 1982.	1-10
A	US, A, 4,663,025 (FU) 05 May 1987.	1-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/11705

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,876,411 (BOWES ET AL.) 24 October 1989.	1-10
A	US, A, 5,112,473 (DAI ET AL.) 12 May 1992.	1-10
A	US, A, 5,254,513 (SHERWOOD, JR. ET AL.) 19 October 1993.	1-10
A,P	US, A, 5,534,135 (DAI ET AL.) 09 July 1996.	1-10